



Changes in Specific Surface as observed by NMR, caused by saturation of Chalk with porewater bearing divalent Ions

Katika, Konstantina; Addassi, Mouadh; Alam, Mohammad Monzurul; Fabricius, Ida Lykke

Published in:
Diffusion Fundamentals

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Katika, K., Addassi, M., Alam, M. M., & Fabricius, I. L. (2014). Changes in Specific Surface as observed by NMR, caused by saturation of Chalk with porewater bearing divalent Ions. *Diffusion Fundamentals*, 22(4), 1-14.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Changes in Specific Surface as observed by NMR, caused by saturation of Chalk with porewater bearing divalent Ions

Konstantina Katika,¹ Mouadh Adassi,¹ M. Monzurul Alam,¹ Ida Lykke Fabricius¹

¹ Technical University of Denmark

Corresponding author: Konstantina Katika, Dept. of Civil Engineering, Technical University of Denmark, Brovej 119, 2800 Lyngby, E-Mail: koka@byg.dtu.dk

Abstract

Nuclear Magnetic Resonance (NMR) spectrometry has proved to be a good technique for determining the petrophysical properties of reservoir rocks; such as porosity and pore size distribution. We investigated how pore water rich in divalent ions affect the NMR signal from chalk with two different depositional textures. We compared two cases. The first experiments on outcrop chalk with high salinity brines showed that saturation with divalent ions (Mg^{2+} , Ca^{2+} and SO_4^{2-}) cause major shifts in the T_2 distribution curve, probably due to precipitation in the pore space. In a second set of experiments, fluid samples where precipitation takes place were found to show shifts in the T_2 relaxation curve due to the creation of crystals. We were able to identify how differences in the rock texture and precipitants within the pore space may affect the transverse relaxation time by altering the surface-to-volume ratio of the pore space. The results of this work could benefit the ongoing study on the optimization of the water composition for Enhanced Oil Recovery (EOR) methods and shed light on how it can affect the mechanical and physical properties of the rock.

Keywords

NMR, transverse relaxation time, chalk, divalent ions, surface-to-volume ratio

1. Introduction

One of the ongoing challenges of the oil and gas research is to enhance the oil recovery by altering the salinity and the composition of the ions in the water used in advanced waterflooding methods. Low salinity flooding has been used in sandstone reservoirs [7] and indications of an effect of divalent ions have been observed in carbonates [1, 8] but the mechanisms behind these observations are poorly understood. By varying the salinity and ionic composition of the brine used for saturation, the mechanism behind pore water action in the chalk can be revealed. Studies have shown that seawater contains divalent ions (calcium, magnesium and sulphate) that are potential determining ions for the chalk surface [6, 8].

Laboratory experiments show that the variation of the salinity and ion concentration can improve the oil recovery in carbonates [9]. But this water injection in carbonates could affect the mechanical properties of the rock. Previous studies have illustrated the effect of the chemical composition of the fluid used for saturation and flooding on the mechanical strength of the chalk [5]. Precipitation reactions that may occur after the injection of water that contain those responsible ions may also affect the mechanical properties of the rock and could damage the contact between the grains of the porous medium [3]. Changes in the grain contact may alter the surface-to-volume ratio of the pore space and thus the relaxation rate. These phenomena create a complex problem that is related to a variety of parameters; temperature and pressure at reservoir conditions, alterations of wettability or chemical processes on the surface of the calcite due to the brine used for the saturation or injection. As a result we need to simplify the system and check the effect of each parameter individually on the porous medium under investigation. Previous work [3] has shown that the potential determining ions Mg^{+2} and Ca^{+2} may change the specific surface of the pore space of the outcrop chalk from Stevns Klint and affect the mechanical properties of the rock. These effects were successfully illustrated in the T_2 distributions of the saturated rock. Checking each of the responsible divalent ions alone could help us identify how each one could affect the pore space stiffness and consequently the surface-to-volume ratio in a carbonate reservoir. This evaluation may lead to better predictions of the reservoir response to water injection.

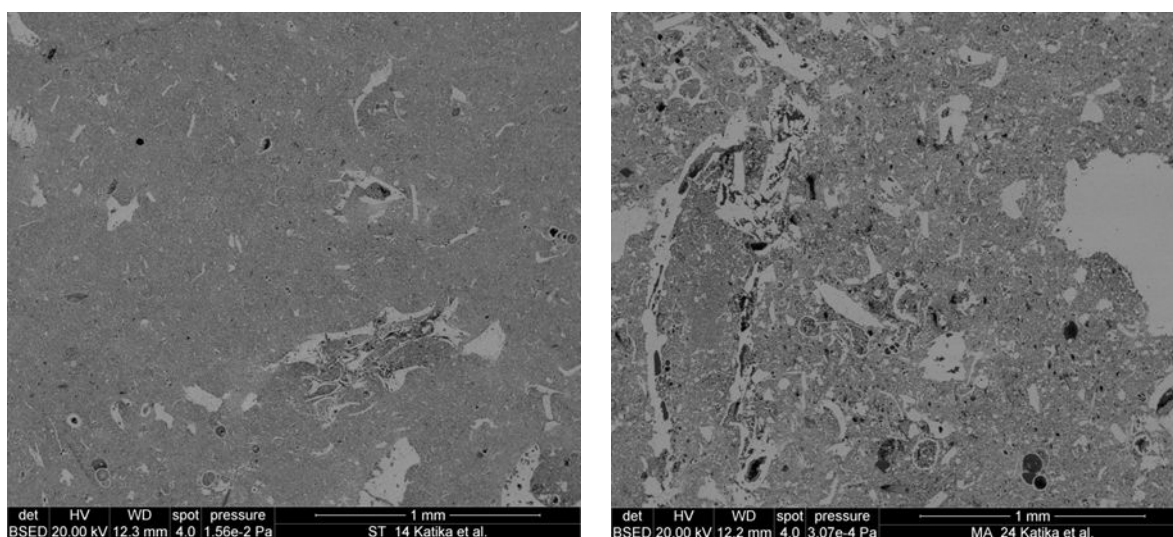


Figure 1. Backscatter electron micrographs of chalk sample from block ST with mudstone texture (left), and chalk sample from block MA with wackestone texture (right).

In the current paper, we present data from petrophysical investigations of outcrop chalk to illustrate the interaction of divalent ions with the surface of this porous medium with the use of low-field NMR. Laboratory experiments and mineralogical investigation were conducted on core plugs saturated with different fluids to evaluate the effect of salinity and specific ions (Mg^{2+} , Ca^{2+} and SO_4^{2-}) on the surface-to-volume ratio of outcrop chalk samples with two different textures (Figure 1). We studied the T_2 relaxation distributions of the fully saturated chalk samples and how they are affected by the presence of individual ions.

2. Theory and Methods

2.1 Rock materials

Outcrop chalk from Stevns Klint near Copenhagen, Denmark, was used for the present study. We obtained two different blocks (MA and ST-block) from the same area but different beds.

The two blocks differ in texture as ST represents carbonate mudstone and MA represents carbonate wackestone (Figure 1).

2.2 Mineralogical Investigation

Table 1. Physical properties of the blocks of outcrop chalk, ST and MA.

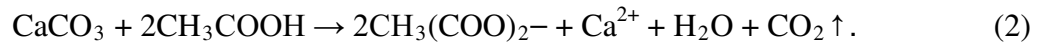
Parameter	ST-Block	MA-Block
Mean value of gas permeability (mD):	6	5
Mean value of porosity (%):	42	38
ρ_2 in water saturated conditions ($\mu\text{m/s}$):	1.5	2.5
Carbonate content (%):	99	99
Specific surface, S_{BET} (m^2/g):	1.7	1.6
Specific Surface of IR, S_{BET} (m^2/g):	50	70

2.2.1 Carbonate content

For the outcrop chalk under investigation, approximately 100 milligrams of each block were crushed in order to specify their carbonate content. The sample was suspended in 250 ml distilled water and 25 ml (± 0.01) of 0.5 N (± 0.001) HCl were added. After 24 hours the solution was boiled on a hot plate for 20 minutes to remove the CO_2 . The solution was then cooled to room temperature. After adding a known amount of phenolphthalein indicator (~ 5 ml), the solution was titrated with NaOH of 0.5 N (± 0.01). The above-mentioned procedure was performed twice for each block and the average results are presented in Table 1.

2.2.2 Collection of Irreducible Residue (IR)

The insoluble residue (IR) in both blocks of outcrop chalk represents all the non-carbonate minerals within our samples. The carbonate was totally dissolved in 2 N CH_3COOH solution at $\text{pH} = 2.23$:



The products of the reaction and excess acetic acid were removed by washing with distilled water. The insoluble residue, that represents 1% of the chalk, was dried at 60°C for 48 hours.

2.2.3 Specific Surface

The specific surface of the samples was obtained with the nitrogen adsorption method, BET [2]. The dry sample had to be partially crushed in order to fit the test tube (~ 5 mm). The same technique was used to acquire the specific surface area of the insoluble residue. The measured specific surface, S_{BET} (m^2/g) was recalculated to specific surface with respect to bulk volume, S_b ($1/\mu\text{m}$), using the following equation:

$$S_b = S_{\text{BET}} \rho_g (1 - \phi), \quad (3)$$

where ϕ is the porosity and ρ_g (g/cm^3) the grain density.

Finally we obtained the specific surface with respect the pore space (Table 2 and 3) by using the following formula:

$$S_\phi = S_b / \phi. \quad (4)$$

Table 2. Core plug properties from the ST-block of outcrop chalk.

Core ID	Bulk volume (cm ³)	Grain density (g/cm ³)	Helium porosity (%)	S_{ϕ} (1/μm)	T_{2-max} (ms)
ST-02	54.67	2.71	42	6.4	117
ST-03	55.03	2.71	42	6.4	100
ST-06	55.54	2.71	41	6.6	105
ST-11	53.34	2.71	42	6.4	110
ST-12	53.68	2.70	42	6.3	105
ST-13	56.26	2.71	41	6.6	100
ST-15	54.81	2.71	42	6.4	64
ST-16	53.81	2.71	43	6.1	66
ST-17	54.96	2.70	43	6.1	70
ST-19	55.53	2.71	43	6.1	143
ST-20	55.29	2.71	42	6.4	145
ST-21	54.26	2.71	41	6.6	146
ST-22	52.68	2.70	41	6.6	138
ST-23	55.55	2.71	43	6.1	137
ST-24	55.07	2.71	43	6.1	140

Table 3. Core plug properties from the MA-block of outcrop chalk.

Core ID	Bulk volume (cm ³)	Grain density (g/cm ³)	Helium porosity (%)	S_{ϕ} (1/μm)	T_{2-max} (ms)
MA-01	52.54	2.71	38	7.1	52
MA-02	50.81	2.71	38	7.1	58
MA-03	53.18	2.70	38	7.0	58
MA-04	51.75	2.70	38	7.0	49
MA-05	50.93	2.70	38	7.0	47
MA-06	51.36	2.70	36	7.7	44
MA-07	50.69	2.70	39	6.8	42
MA-09	50.37	2.70	38	7.0	42
MA-10	50.04	2.70	37	7.4	38
MA-14	51.98	2.70	37	7.4	49
MA-15	49.66	2.70	38	7.0	61
MA-16	50.22	2.70	38	7.0	49
MA-17	51.16	2.70	37	7.4	58
MA-18	50.35	2.70	38	7.0	58
MA-19	51.14	2.70	38	7.0	58

2.3 Porosity and permeability measurements

After drilling the core plugs, they were dried for 4 days at 55°C; helium porosity and gas permeability were measured (Tables 2 and 3). The bulk volume of the samples was determined with the use of Archimedes' method using mercury immersion. The calliper was also used to measure the length and diameter of the samples so as to confirm the evaluated bulk volume. The two results were in good agreement.

2.4 Saturation

Samples were placed in desiccator and vacuum was created by a water pump while brine was poured into the desiccator gradually until the samples were covered with brine. After one week the achieved level of saturation was calculated for each core plug. The degree of saturation was determined using the dry weight, the saturated weight, grain volume by helium expansion and brine density. The density of the brines was measured using a digital density meter of high accuracy ($\pm 0.001 \text{ g/cm}^3$). The achieved level of saturation is shown in Table 4.

2.5 Nuclear Magnetic Resonance

Low-field NMR is a technique commonly used in petrophysical logging and core analysis. It involves a series of manipulations of the hydrogen (^1H) nuclei, which are abundant in both water and hydrocarbons.

The NMR measurements consist of the alignment of the hydrogen nucleus (proton) with the use of static and oscillating magnetic fields and their relaxation after the removal of the second field. T_2 is a characteristic time that represents the decay of the protons within the fluid after their polarization. The T_2 decay time is a function of the distance of the protons from the surface walls, fluid properties (hydrogen index, viscosity, ionic composition), formation mineralogy and molecular diffusion.

After each NMR measurement, an inversion technique converts the decay curves into a T_2 spectrum. The relaxation of protons close to the solid surface is faster than that of the protons in the free flowing fluid [4]. The T_2 relaxations were measured using the Carr, Purcel, Meiboom, Gill (CPMG) pulse sequence. With the use of a CPMG pulse sequence, effects of magnetic gradients can be minimized and therefore relaxation due to diffusion is negligible. Assuming that the bulk fluid relaxation is slow compared to surface relaxation, the relaxation rate, $1/T_2$ (1/ms), in these NMR experiments is proportional to the surface-to-volume ratio, S/V (1/ μm) of the pore space, and the surface relaxivity, ρ_2 ($\mu\text{m/s}$), in a homogenous porous system [4]:

$$\frac{1}{T_2} = \rho_2 \frac{S}{V}. \quad (5)$$

The surface-to-volume ratio represents the specific surface of the pore space, S_ϕ (1/ μm), hence the above-mentioned equation could be written as follows:

$$\frac{1}{T_2} = \rho_2 S_\phi. \quad (6)$$

If we assume the surface relaxivity constant, then the transverse relaxation time is very sensitive to changes in the surface-to-volume ratio of the porous medium. The specific surface of the pore space of the chalk under investigation, S_ϕ (1/ μm), was measured by nitrogen adsorption, BET, and the T_2 in equations (5) and (6) represents the value of T_2 at maximum amplitude; hence we obtained the surface relaxivity.

In the present study, NMR measurements were made using a GeoSpec2 NMR Core Analyzer at 2.25MHz, 35°C and atmospheric pressure.. The T_2 relaxation spectra were generated using the WinDXP (Oxford Instruments, UK) software. All measurements were conducted at high Signal to Noise Ratio ($SNR > 200$) for bigger reliability of our results. The recycle delay (repetition time) was selected at 40s, number of echoes at 16000, and the CPMG inter echo spacing (τ) at 50 μs . The $\pi/2$ and π pulses were 9.75 μs and 19.5 μs , respectively.

2.6 Chalk samples and brine

Fifteen cylindrical samples from each block were collected and divided into groups of six and then saturated with five different aqueous solutions (deionized water, sodium chloride solution, magnesium chloride solution, calcium chloride solution and sodium sulfate solution). The concentration of the salts (NaCl , MgCl_2 , CaCl_2 and Na_2SO_4) in each solution is selected so as to maintain the same ionic strength (1.83 mol/L) in all cases. The selection of multiple plugs allowed us to verify the repeatability of our results.

Table 4. Saturation of core plugs.

Core ID	Brine used for saturation	Conc. (g/L)	Fluid density (g/cm^3)	Saturation (%)	Core ID	Brine used for saturation	Conc. (g/L)	Fluid density (g/cm^3)	Saturation (%)
ST-02	Deionized water	-	0.9973	96	MA-01	Deionized water	-	0.9973	99
ST-03				96	MA-02				100
ST-06				96	MA-03				99
ST-11	NaCl solution	100	1.0687	97	MA-04	NaCl solution	100	1.0687	99
ST-12				95	MA-05				97
ST-13				95	MA-09				99
ST-15	MgCl ₂ solution	58	1.0436	95	MA-06	MgCl ₂ solution	58	1.0436	97
ST-16				95	MA-09				99
ST-17				95	MA-10				98
ST-19	CaCl ₂ solution	68	1.0492	97	MA-14	CaCl ₂ solution	68	1.0492	98
ST-20				96	MA-15				97
ST-21				99	MA-16				98
ST-22	Na ₂ SO ₄ solution	87	1.0711	100	MA-17	Na ₂ SO ₄ solution	87	1.0711	96
ST-23				97	MA-18				100
ST-24				95	MA-19				99

Table 5. Physical properties and information concerning the saturation of the samples saturated with calcite equilibrated water.

Core ID	Bulk volume (cm^3)	Grain density (g/cm^3)	Helium porosity (%)	S_ϕ ($1/\mu\text{m}$)	Fluid density (g/cm^3)	Saturation (%)	$T_{2\text{max}}$ (ms)	ρ_2 ($\mu\text{m/s}$)
ST-07	56.21	2.71	42	6.4		95	106	1.5
ST-08	55.02	2.71	42	6.4	0.9974	95	106	1.5
ST-09	54.70	2.71	42	6.4		95	121	1.3

For the preparation of the brines, which were used for the saturation, all salts used were dissolved in calcite equilibrated water. For the equilibrated calcite solution, synthetic CaCO_3 (>98% CaCO_3 , 10 microns) was used. Approximately 50 grams of this powder was poured into a beaker containing five liters of deionized water. The solution remained on the stirrer at room temperature ($\sim 20^\circ\text{C}$) and equilibrated with atmospheric $\text{CO}_{2(\text{g})}$ until the calcite concentration indicates that it is equilibrated. The concentration at this stage was 24 ppm. For the preparation of the brines all salts used were dissolved in the calcite equilibrated water

(Table 4). In addition to the cases of saturation presented above, three more plugs were saturated with calcite equilibrated water (24ppm) to illustrate that this brine does not affect the T_2 relaxation time on chalk. Information concerning the physical properties and the saturation of those samples is given in Table 5.

While preparing the magnesium and calcium solution for the saturation, in which we mixed MgCl_2 and CaCl_2 salts with calcite equilibrated water, we observed their reaction with the use of low field NMR. Two samples were prepared and their T_2 relaxation was measured every few hours, till a shift to lower relaxation times occurred due to a precipitation reaction that took place within the solution. In the case of the Ca-rich brine a few crystals were visible in the bottom of the beaker where the salt was mixed with the calcite carbonate equilibrated water a few minutes after the dissolution of the salt. The results of those measurements are shown in Figure 2. In both samples the T_2 distribution stopped shifting to lower times after 100 hours. The shift of the T_2 curve happened faster for the case of the Ca-rich brine. Since these brines were later used for the saturation of our samples they were filtered in order to remove as many precipitants as possible. Further precipitation took place in the solutions, after they spent seven days under vacuum conditions along with the chalk samples during the saturation.

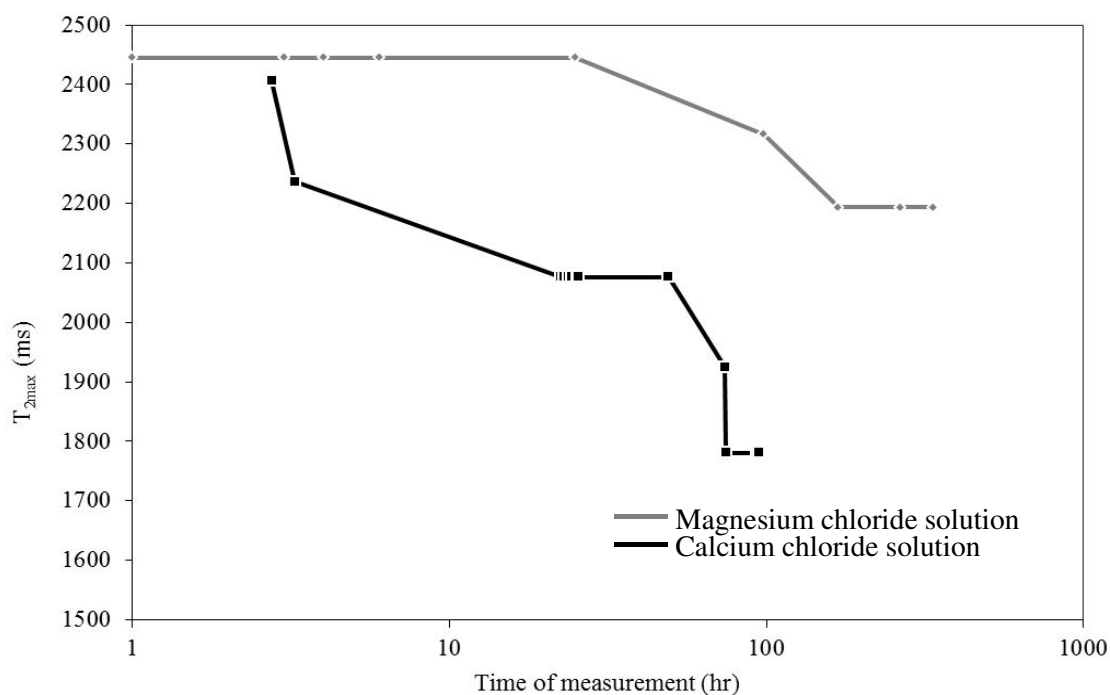


Figure 2. Observed precipitation reaction for the cases of MgCl_2 and CaCl_2 dissolved in the calcite equilibrated water. On the y-axis is shown the maximum value of the T_2 distribution for every measurement. On the x-axis it is the time of each measurement; the solution was prepared at time zero, while it required approximately 15 minutes to finish the first NMR measurement.

Low field NMR measurements were performed on the brines used for the saturation, after they spend seven days in vacuum conditions along with the chalk samples. In addition to those brines we prepared similar brines (sodium chloride solution, magnesium chloride solution, calcium chloride solution and sodium sulphate solution) with the same ionic strength (1.83 mol/L) but this time the salts were dissolved in deionized water.

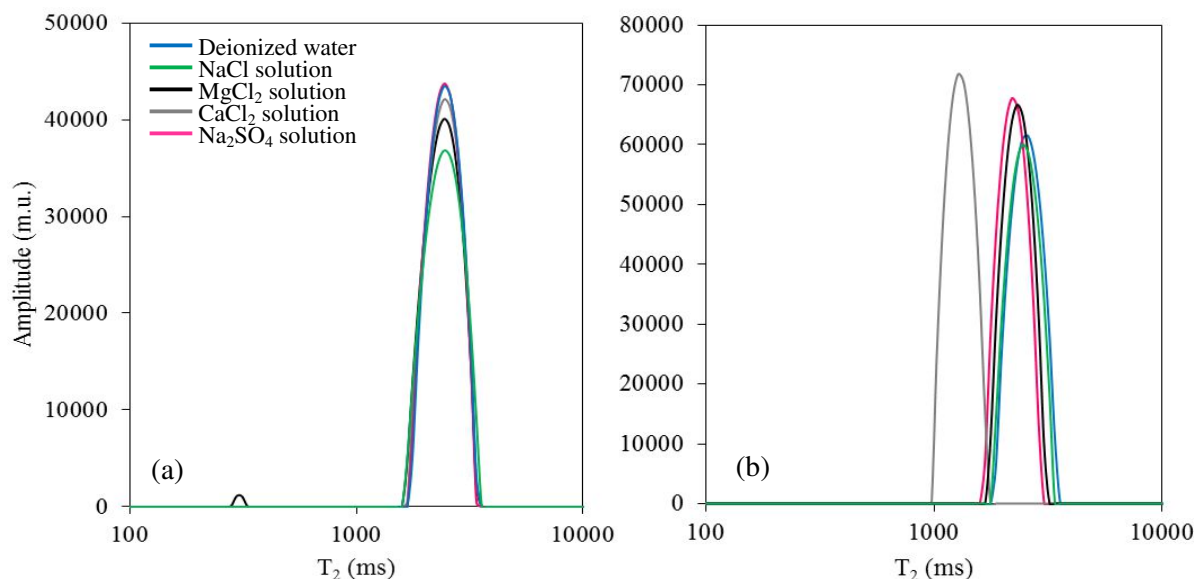


Figure 3. The T_2 relaxation of (a) 20 ml fluid samples of the solutions based in deionized water and (b) 30 ml fluid samples of the solutions used for the saturation. In case (a) no carbonates are present inside the fluid. In case (b) the salts were dissolved in water that contained calcium and carbonate ions and they spent seven days under vacuum conditions with the chalk for the saturation. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis.

3. Results

3.1 Brines before and after contact with chalk

Figure 3 presents the T_2 distribution of the brines prepared with deionized water and after these brines spent seven days along with the chalk samples during the saturation. Figure 3 illustrates that when no precipitation took place the T_2 curve of the brine is always similar to the T_2 curve of the deionized water. In the cases of sodium chloride solutions and when the salts of $MgCl_2$, $CaCl_2$ and Na_2SO_4 were dissolved in deionized water, there is no extra surface inside the fluids to speed up the relaxation. Changes in the amplitude of those curves are due to changes in the amount of water molecules within the samples. When $MgCl_2$, $CaCl_2$ and Na_2SO_4 were mixed with calcium carbonate equilibrated water, the NMR signal shifted to low T_2 (Fig. 3a).

3.2 Outcrop chalk saturated with divalent ions (ST-block)

Figure 4 presents all the T_2 distributions obtained from the plugs from the ST-block after the saturation. The repeatability among the measurements is illustrated in the same figure since for each case of saturation all three plugs gave similar results. In Figure 5 we present the average of the three curves of each case in one so as to illustrate the effect of the deionized water and each ion (Na^{+1} , Mg^{+2} , Ca^{+2} and SO_4^{-2}) on outcrop chalk. From the T_2 distributions we can observe that saturation with deionized water, Ca-equilibrated water and sodium chloride rich water results in similar T_2 -distribution. By contrast saturation with Mg-rich brines leads to faster relaxation of the protons and saturation with Ca and SO_4 -rich brines leads to slower relaxation than the deionized water.

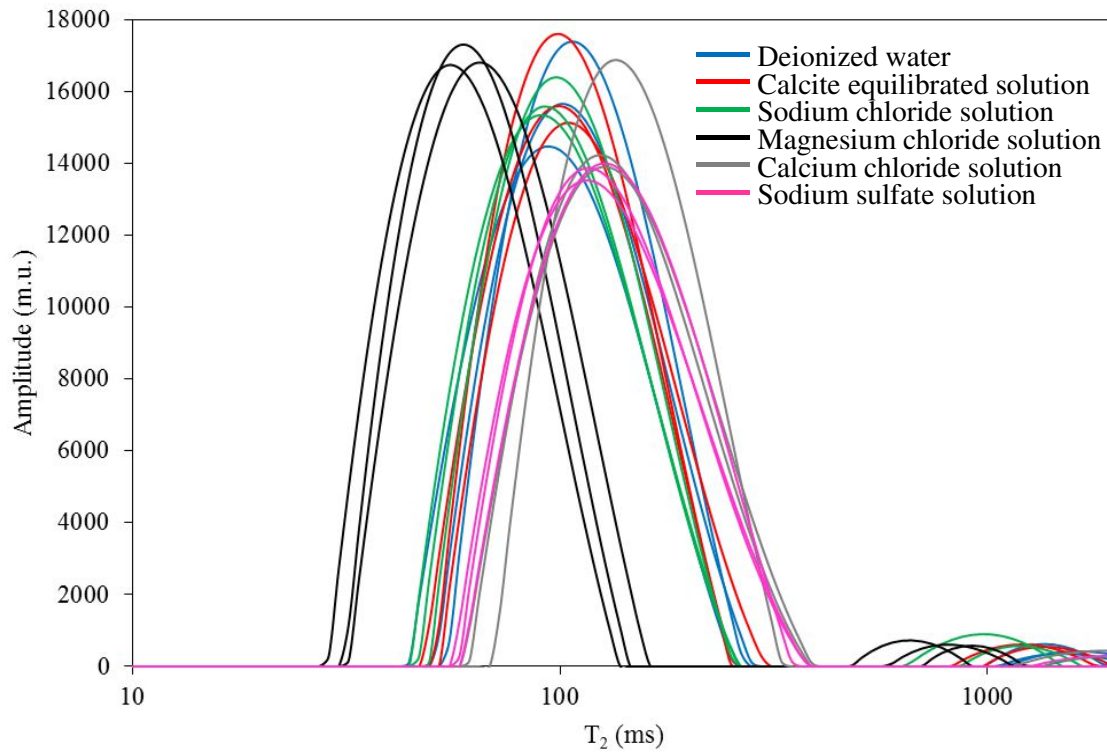


Figure 4: The T_2 distribution of the saturated ST-plugs. Different colours represent saturation with each of the solutions. The three lines of the same colour represent the three different samples saturated with the same solution. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis. A clear representation of Figure 4 is shown in Figure 5 where the average lines are illustrated.

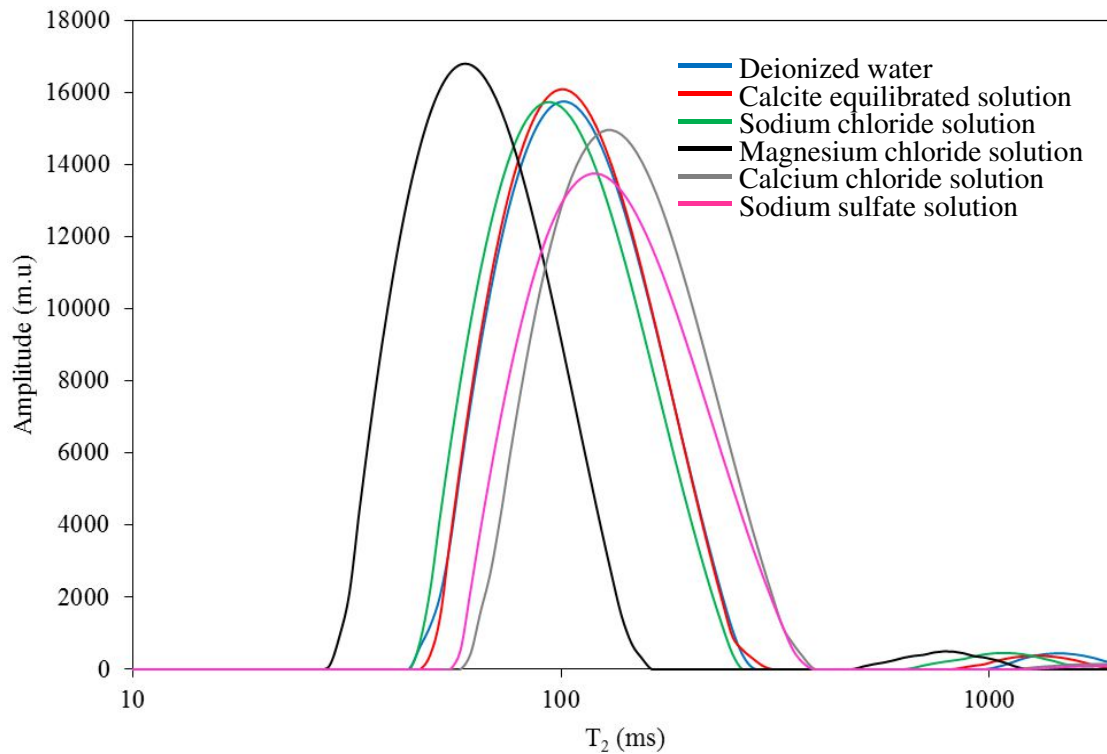


Figure 5: The average T_2 distribution of the saturated ST-rocks. Each of the lines represents the average line of the three cases with the same colour from Figure 4. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis.

3.3 Outcrop chalk with high surface-to-volume ratio saturated with divalent ions (MA-samples)

Figure 6 presents all the T_2 distributions obtained from the plugs from the MA-block after the saturation. From those curves we can identify two connected pore spaces. The first peak of those curves represents the typical pore space of chalk; just a few micrometres, and the second peak represents the relaxation of the fluid that exists in intra fossil porosity. In that case the fluid is freer and requires longer time to relax.

Again, the derived curves for each saturation match, so we illustrate their average distributions in Figure 7. From the derived average T_2 curves we can conclude that saturation with Mg-rich brines leads to faster relaxation of the protons than Ca and SO_4 -rich brines.

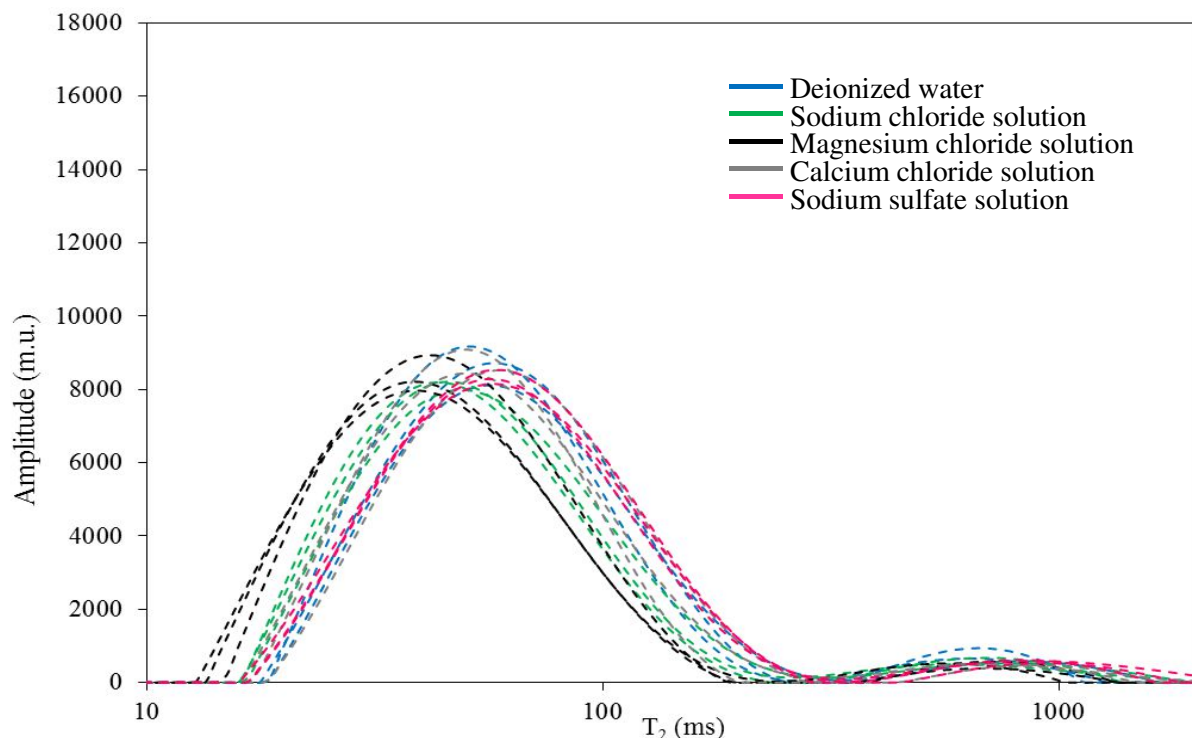


Figure 6: The T_2 distribution of the saturated MA-plugs. Different colours represent saturation with each of the solutions. The three lines of the same colour represent the three samples saturated with the same solution. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis. A clear representation of Figure 6 is shown in Figure 7 where the average lines are illustrated.

4. Discussion

The T_2 distributions of the brines used for the saturation show that excess surface is generated in the fluid when magnesium, calcium and sulphate ions are in contact with the free carbonates that exist in the calcite equilibrated water (Fig. 3). This excess surface increased the surface-to-volume ratio and as a result the relaxation rate increased as well since the surface relaxivity is always the same for the bulk fluid in equation (6). The water close to the surface of the precipitants obtains faster relaxation than the free fluid. The T_2 distributions show that even the smallest amount of calcium and carbonate in the water can contribute to the creation of magnesium- and calcium carbonates as well as calcium sulphate that are responsible for the creation of excess specific surface within the fluid.

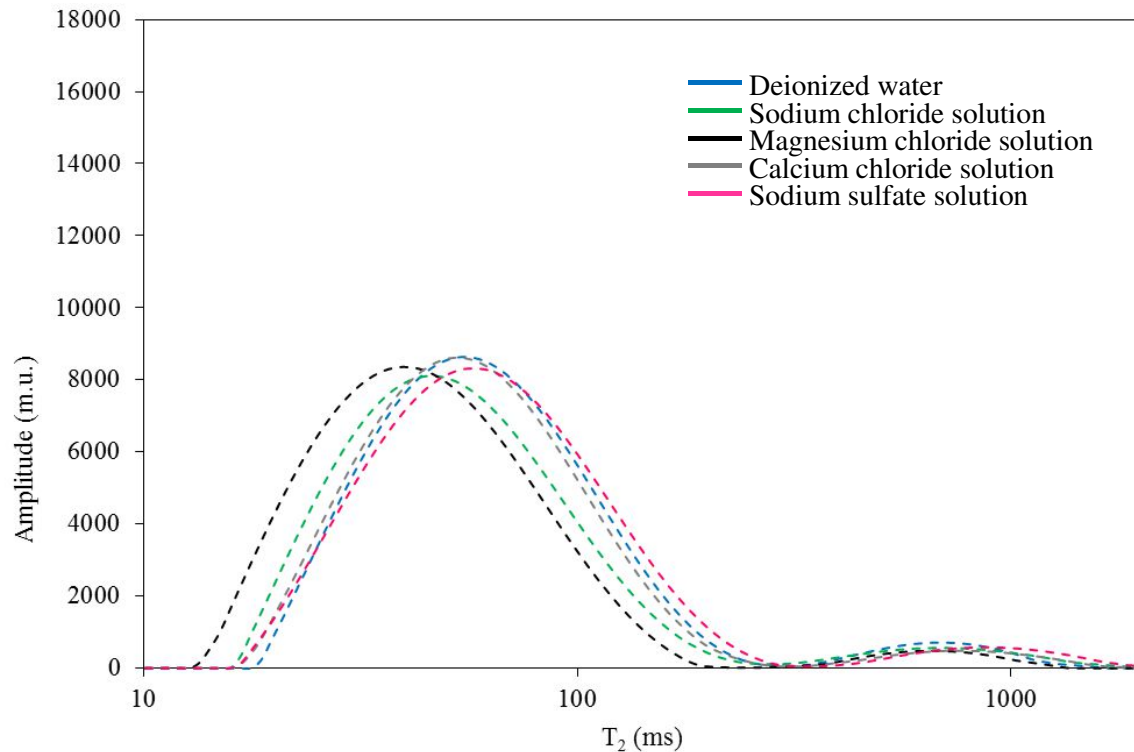


Figure 7: The average T_2 distribution of the saturated MA-samples. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis.

Checking the signal of the brines in Figure 3, we can observe that the precipitants within the calcium chloride solution lead to faster relaxation than the precipitants within the magnesium chloride solution. This could be an indication of their quantity; more and smaller precipitants create more surface within the bulk fluid causing the molecules to relax faster.

As concluded in earlier studies [3, 5], saturation of carbonates with divalent ions as Mg^{+2} and Ca^{+2} leads to precipitation reactions that might change the surface-to-volume ratio and as a result affect the T_2 relaxation time. As shown in Table 2 and 3, we measured the specific surface at dry conditions and used the porosity, and grain density to get the surface-to-volume ratio of the porous medium. For the samples that were later fully saturated with deionized water, NMR measurements were performed and we were able to obtain the T_{2max} . Using this value and the surface-to-volume ratio in dry conditions and equation (6) we obtained the surface relaxivity. This value is independent of any surface reactions that may have occurred after the saturation. If we consider that the surface relaxivity does not change after the saturation, and the shifts in the T_2 distribution are only due to changes in the surface-to-volume ratio we can calculate the specific surface of the plugs after the saturation with divalent ions. We consider, $\rho_2 = 1.5 \mu m/s$ for the ST-samples and $\rho_2 = 2.5 \mu m/s$ for the MA-samples after the saturation and using equation (6) we recalculate the specific surface of the pore space as presented in Table 6.

As observed the surface-to-volume ratio increases in all cases after the saturation with Mg-rich brines while reduces after the saturation with Ca and SO_4 -rich brines. Possibly the precipitants of magnesium carbonates remain in the pore space of the medium increasing the specific surface, while the calcium and sulfate cover the surface of the grains and as a result reduce the specific surface.

Table 6. Surface-to-volume ratio after the saturation if the surface relaxivity is not affected by the presence of divalent ions.

Core ID	Brine used for saturation	S_ϕ in dry conditions (1/ μm)	S_ϕ in wet conditions (1/ μm)	Core ID	Brine used for saturation	S_ϕ in dry conditions (1/ μm)	S_ϕ in wet conditions (1/ μm)
$\rho_2=1.5 \mu\text{m/s}$				$\rho_2=2.5 \mu\text{m/s}$			
ST-15	MgCl ₂ solution	6.2	11.1	MA-06	MgCl ₂ solution	6.9	9.5
ST-16		6.1	10.7	MA-09		7.1	9.5
ST-17		6.1	10.1	MA-10		7.2	10.6
ST-19	CaCl ₂ solution	6.1	5.0	MA-14	CaCl ₂ solution	7.2	8.1
ST-20		6.2	4.9	MA-15		7.1	6.5
ST-21		6.4	4.9	MA-16		7.1	8.1
ST-22	Na ₂ SO ₄ solution	6.4	5.1	MA-17	Na ₂ SO ₄ solution	7.2	6.9
ST-23		6.1	5.2	MA-18		7.0	6.9
ST-24		6.1	5.1	MA-19		7.0	6.9

In Figure 8 we compare the case studies of ST and MA-samples under investigation. The area under the curve that represents the porosity of the samples remains similar, since it corresponds to ~38% and ~42% respectively, but the T_2 curves for MA-samples are broader and shifted to lower relaxation times. In Table 1 we presented the surface relaxivity of those blocks, and although the specific surface is comparable, MA-samples have a larger surface relaxivity than the ST-samples. The specific surface of the non-carbonate components of the MA-block is approximately 1.5 times higher than the one of the ST-block (Table 1). The MA-samples thus have a broader pore-size distribution than the ST-samples, so that the use of the T_2 peak for calculating ρ_2 for MA samples may give less reliable results than in the case of ST-samples where the T_2 peak is narrow.

5. Conclusions

Low field NMR was successfully used to identify changes in the surface-to-volume ratio of outcrop chalk after the saturation with brines containing divalent ions. The same technique was also used successfully to detect the precipitation reactions that occurred among the magnesium, calcium and sulfate ions and the carbonates.

In the NMR experiments conducted in this study the relaxation rate was significantly affected by changes in the surface-to-volume ratio when the surface relaxivity was assumed constant. Chalk saturated with Mg-rich brines resulted in a shift to low T_2 , indicating precipitation within the pore space of the medium that increases the specific surface of the pore space. The precipitation reaction between calcium and sulfate ions and carbonates led to an increase in T_2 , probably resulting from coating of the calcite crystals of the chalk and the resulting reduction of the specific surface of the pore space. Two different blocks of chalk with different texture illustrate how T_2 relaxation time varies as a result of different pore size distribution.

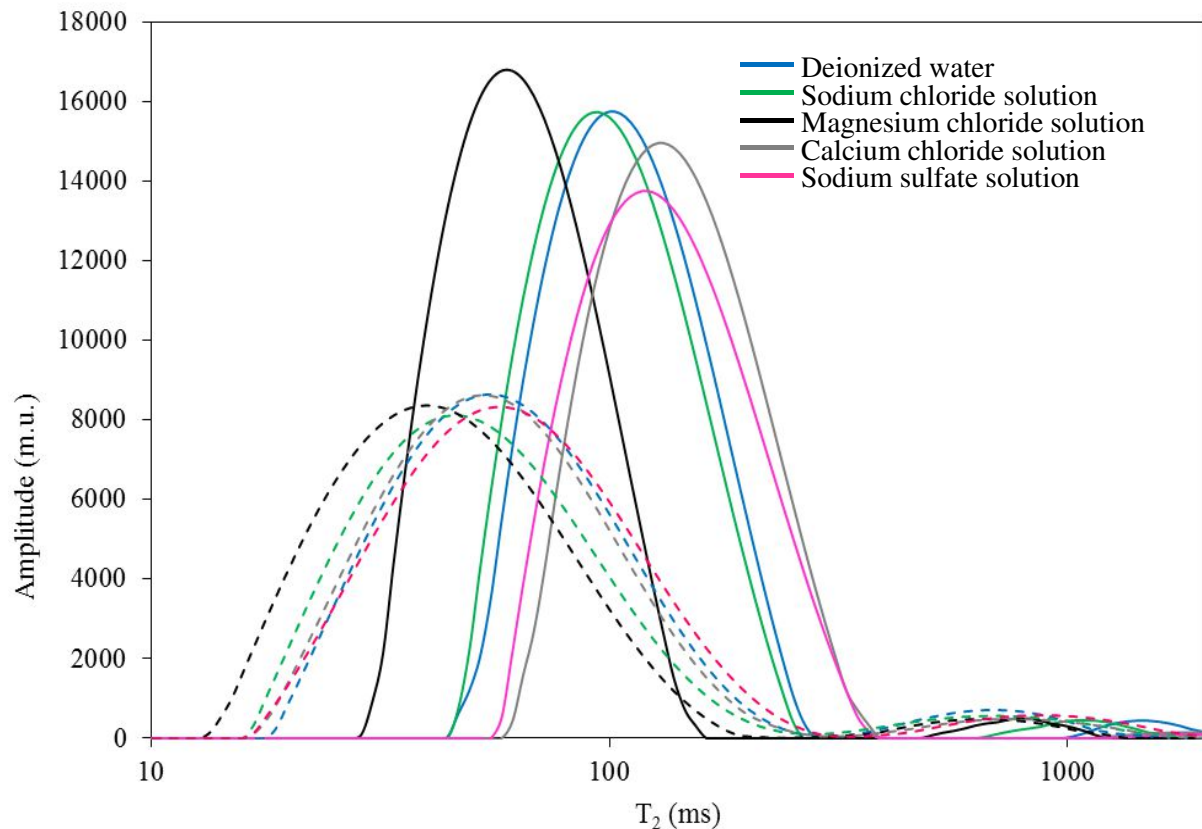


Figure 8: Comparison of the average T_2 distributions of the saturated ST and MA-samples. The T_2 relaxation time is given in milliseconds on the x-axis while the amplitude is normalized in machine units on the y-axis.

Acknowledgments

The authors wish to thank the Danish Energy Agency, Mærsk Oil and DONG Energy for funding the research.

References

- [1] Austad, T., Strand S., Madland M. V., Puntervold T., and Korsnes I. R.: Seawater in Chalk: An EOR and Compaction Fluid, SPE Reservoir Evaluation and Engineering, 11 (4), 648-654, (2007).
- [2] Brunauer, S., Emmett, P. H., and Teller, E., 1938, Adsorption of gases in multimolecular layers: Journal of the American Chemical Society, 60(2), 309-319.
- [3] Katika K., Alam M. M. and Fabricius I. L.: Nuclear magnetic resonance and sound velocity measurements of chalk saturated with magnesium rich brine, Poromechanics V, 678-684, (2013).
- [4] Kenyon, W. E., Petrophysical principles of applications of NMR logging: Log Analyst, 38, 21-43, (1997).
- [5] Madland M. V., Hiorth A., Omdal E., Megawati M., Hildebrand-Habel T., Korsnes I. R., Eyje S., Cathles M. L.: Chemical Alterations Induced by Rock-Fluid Interactions When Injecting Brines in High Porosity Chalks, Transp Porous Med, 87, 679-702, (2011).
- [6] Pierre A., Lamarche J. M., Mercier R. and Foissy A.: Calcium as potential determining ion in aqueous calcite suspensions, Journal of Dispersion Science and Technology, Vol. 11, Issue 6, 611-635, (1990).

- [7] Seccompe C. J., Lager A., Webb K., Jerauld G. and Fueng E., 2008: Improving Waterflood Recovery: LoSalTM EOR Field Evaluation, SPE 113480, presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 19-23 April.
- [8] Strand S., Høghesen J. E. and Austad T.: Wettability alteration of carbonates-Effects of potential determining ions (Ca^{2+} and SO_4^{2-}) and temperature, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 275 (1–3), 1–10, (2006).
- [9] Webb, K. J.; Black, C. J. J.; Tjetland, G.: A Laboratory Study Investigating Methods for Improving Oil Recovery in Carbonates, presented at International Petroleum Technology Conference, Doha, Qatar, 2005.